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Microwave Spectrum and Barrier to Internal Rotation in Trifluoronitromethane*

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The microwave spectrum for CF_3NO_2 has been observed for the $J=1\rightarrow J=2$ through the $J=4\rightarrow J=5$ transitions. Some 35 lines in these transitions are assigned, and the Stark effects for three of these were studied quantitatively and interpreted. A discrepancy in the Stark effect of a $4\rightarrow5$ transition can be accounted for by properly adjusting the sixfold barrier to internal rotation. The parameters used to obtain the best fit for the spectrum are the following: $B+C=4917.4\pm0.4$ Mc/sec, $B-C=453.9\pm5$ Mc/sec, $A(NO_2)=13205\pm150$ Mc/sec, $A(CF_3)=5700$ Mc/sec (assumed), $V_6=780\,000$ Mc/sec$=74.4\pm5$ cal/mole. The dipole moment obtained from the Stark-effect measurements is 1.44 ± 0.03 D.

INTRODUCTION

IT is reasonable to expect the structure of trifluoronitromethane to be similar to nitromethane and methyl boron difluoride. That is, all would have a symmetrical threefold rotor (CH_3 or CF_3) attached to a twofold symmetrical frame (NO_2 or BF_2), thus giving a sixfold barrier to internal rotation. Because of the high multiplicity it is customary to expect a low barrier. Nitromethane has a barrier of 6.03 cal/mole[1] and methyl boron difluoride has a barrier of 13.77 cal/mole.[2] On this basis it might be expected that the barrier to internal rotation in trifluoronitromethane will be low also.

Recently, Karle and Karle[3] have reported the results of an electron-diffraction study of CF_3NO_2 and similar molecules. They report their data as indicating that the NO_2 group is bent so as to give a staggered ethane-type configuration with one position missing. Their interpretation gives an angle of noncoplanarity of $9°35'\pm1°$, and they report two thirds of the molecules to be in a staggered configuration and one third in an eclipsed configuration. From the root-mean-square amplitude of vibration of the O–F distance they determine a potential barrier to internal rotation of 3 kcal/mole. The potential barrier used was sixfold with the three minima of the staggered configuration being lower than the three minima of the eclipsed.

These conclusions are in conflict with the idea (see Ref. 1) that barriers to internal rotation may be expressed as a rapidly convergent Fourier series with all terms but the threefold being very small.

It should also be noted that CF_3NO_2[4] may convert from an existing staggered to an eclipsed configuration by either a rotation of the CF_3 group or an inversion of the NO_2 group through a plane containing the C–N bond. This inversion motion would be a vibration with a double minimum.

Both the motion of inversion and internal rotation would take place with the movement of the two oxygens alone (relative to the CF_3N frame). For an angle of noncoplanarity of $9°35'\pm1°$, as given by electron diffraction, the oxygen would have to move less than 0.2 Å to pass from one minimum to the other if the motion were inversion; whereas, if the motion were internal rotation, the oxygens would have to move more than 1 Å to go from one minimum to the next nearest minimum. If the observed motion is internal rotation the effective barrier to inversion must be high. Since the barrier to inversion is much thinner (less than 0.2 Å) than the barrier to internal rotation (more than 1 Å) then it must be considerably higher. In the WKB approximation it would have to be 1.0/0.2 or five times as high to be equivalent. Since even a 3-kcal[5] barrier separating minima 0.2 Å apart would require slopes of the potential function which are much higher than the forces usually reported for similar motions, we believe there must be an alternate explanation for the electron-diffraction data.

The results of our observations on the microwave spectrum are in conflict with any model with a high barrier for internal rotation or for inversion of the NO_2 group.

The initial observations[6] on the microwave spectrum shows that the pattern of observed lines is very complex

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[1] E. Tannenbaum, R. J. Myers, and W. D. Gwinn, J. Chem. Phys. **25**, 42 (1956).

[2] R. E. Naylor and E. B. Wilson, J. Chem. Phys. **26**, 1057 (1957).

[3] I. L. Karle and J. Karle, J. Chem. Phys. **36**, 1969 (1962).

[4] It should be made clear that all discussion of inversion of the NO_2 group is our interpretation of the consequence of the Karle and Karle model. They did not discuss this facet of the problem.

[5] See, for example, L. I. Shiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), pp. 184–195.

[6] E. Tannenbaum, R. J. Myers, and W. D. Gwinn, Symposium on Molecular Spectra and Molecular Structure, Ohio State University, Columbus, Ohio, 1955.

and similar in many respects to that of nitromethane. This is in conflict with the proposal of a high barrier for this molecule. In comparison with nitromethane, the CF_3 group has a much higher moment of inertia than a CH_3 group. If the barrier were as high as 3000 cal (or even 1000 cal), the low-lying internal-rotation levels would appear in a rigid-rotor pattern without even the A–E splittings characteristic of an intermediate barrier. There would be weaker transitions arising from higher internal rotation levels which would show A–E splittings, and still higher levels would have the pattern of a nearly free rotor. The intensities of these lines in the microwave spectrum would be so low because of the low thermal populations of these excited levels that they could only be noticed by a careful search. The general appearance of the strong lines of the spectrum would be that of a rigid rotor.

Such is not the case with trifluoronitromethane. The pattern of each $J \rightarrow J+1$ transition is that of a strong central complex of many lines with many satellites on either side of this central pattern. The greatest intensity of lines is in the central portion of each complex, those representing the nearly free rotor spectrum of the higher excited states.

The spectrum of CF_3NO_2 was first investigated in 1955.[5] At this time calculations were quite difficult and the assignment questionable. An upper limit of 40 cal/mole was assigned to the barrier. Because of the larger moment of inertia of the CF_3 group and a barrier higher than nitromethane, computations using a desk calculator were not adequate, as they had been for the spectrum of nitromethane. The present availability of large computers along with improved spectrometer equipment[7] made a reinvestigation of the problem possible.

CALCULATION OF SPECTRA

The matrix elements used for this calculation have been previously reported.[1,8] Using the notation of Ref. 1, the variables involved are the following: $B+C$, $B-C$, $A(NO_2)$, $A(CF_3)$, and V_6, where B and C are the rotational constants of the molecule along the appropriate axes, $A(NO_2)$ and $A(CF_3)$ are the rotational constants of the NO_2 group and the CF_3 group respectively along the molecular axis of symmetry, and V_6 is the sixfold barrier to internal rotation.

A computer routine was written to construct a matrix with the proper elements; diagonalization was accomplished by the Jacobi method. Transformation of the direction-cosine matrix then allowed a calculation of the selection rules, line intensities, and Stark effect. This was all accomplished in the computer, the output giving the spectrum to be expected.

The energy matrix may be factored into six submatrices due to the fact that matrix elements connect only k_1 to $k_1 \pm 6$ levels, where k_1 is the quantum number for the rotation of the CF_3 top along the molecular axis. Two of these submatrices are nondegenerate, and there are two doubly degenerate submatrices. If we designate each submatrix by the symbol β, equal to the lowest positive value of k_1 in the respective submatrix, the six submatrices are $\beta=0$, 1, 2, 3, 4, and 5. The singly degenerate submatrices are $\beta=0$ and $\beta=3$; the doubly degenerate sets are $\beta=2$, 4 and $\beta=1$, 5. The energy matrix must be calculated for each of these four submatrices for each spectrum desired. Further factorization into K even and K odd matrices is possible because of matrix elements of the type

$$(J, K, k_1 \mid H \mid J, K \pm 2, k_1').$$

As a result of the zero nuclear spin of the two equivalent oxygens, β must be even for K even, and odd for K odd.

The values of k_1 are not bounded, and it was necessary to truncate the infinite matrices in order to diagonalize them. It was found that by using values of k_1 from -27 to $+27$ the microwave lines of interest could be predicted to reasonable accuracy—better than 1 part in 10^6. Calculation of the Stark effect of the spectrum up to $J=5$ required a diagonalization of the matrix for $J=6$ levels. Even with the factorization and truncation mentioned above, one must diagonalize two 63×63 and two 54×54 matrices for the $J=6$ level alone. Calculation of the full spectrum up to $J=6$ required 30 min to 1 h of computer time on the IBM 7090 or the CDC 1604.

Diagonalization of the matrices was carried out in double precision on the IBM 7090 (36-bit work length). Computations using the CDC 1604 were made in single precision, since the longer word length (48 bit) was adequate to make the floating-point round-off error less than 1 part in 10^7.

The resulting eigenvectors indicated that in most cases the initial basis functions are extensively mixed for the final energy levels and that the original quantum numbers K and k_1 are no longer good quantum numbers. We have, therefore, used the pseudoquantum number I, to represent the ordering of the energy levels of each submatrix in question. The submatrices are labeled as $\beta=0$, 1, 2 or 3, where $\beta=1$ also implies the $\beta=5$ matrix, the other member of the degenerate pair. Likewise, $\beta=2$ also implies the $\beta=4$ matrix.

ASSIGNMENT

The spectrum of a sixfold rotor with a low barrier to internal rotation, such as CH_3NO_2, consists of groups of transitions falling at regular intervals of approximately $(B+C)(J+1)$. Many lines in each group are split from the center of each of these transitions; the amount of splitting depends upon the other parameters. In general, the lower k_1 lines are split the furthest, and

[7] A. Narath and W. D. Gwinn, Rev. Sci. Instr. **33**, 79 (1962).
[8] E. B. Wilson, C. C. Lin, and D. R. Lide, J. Chem. Phys. **23**, 136 (1955).

lines having higher k_1 pile up at a multiple of $B+C$. In nitromethane this pile-up was not very marked because the energy levels belonging to higher k_1 values were so high in energy that they were sparsely populated and the corresponding lines were too weak to be observed. In nitromethane, lines with k_1 greater than 7 were too weak to be observed, but in trifluoronitromethane this limit was between $k_1=20$ to 30. This means that for trifluoronitromethane the intensities are distributed among many more transitions.

The general shape of each transition can be compared with calculations and it was observed that the molecule definitely exhibited a low-barrier spectrum. A barrier of 500 cal/mole or more would have resulted in lines split from the center further than we observed, and the pile-up at the center of each $J\rightarrow J+1$ transition would not have been observed.

The pile-up of lines was observed for the $J=1\rightarrow 2$ through the $J=4\rightarrow 5$ transitions. For the higher J transitions lines as far as 50 Mc/sec from the center of the transition were obscured by this grouping of higher k_1 lines. These lines occurred at regular multiples of 4916 Mc/sec, so this number was initially taken to be a measure of $B+C$. Refinements were made later to this value to improve the agreement of observed vs calculated lines.

The spectrum is quite insensitive to the value of $A(CF_3)$ and because of this a reasonable value of this parameter was chosen to be 5700 Mc/sec and held constant throughout the calculations. If the NO_2 group is assumed to be coplanar with the carbon atom, there is a relationship between $B+C$, $B-C$, and $A(NO)_2$. Using the assumption that $I_A(NO)_2=I_C-I_B$, then $A(NO_2)$ is determined as a function of $B+C$ and $B-C$. The problem thus reduces to a determination of two parameters. It was convenient to choose the two parameters to be $A(NO_2)$ and V_6. Summarizing, $B+C$ was determined from the center of the grouping of lines initially, $A(CF_3)$ was assumed, and $B-C$ is determined as a function of $B+C$ and $A(NO_2)$ assuming no inertial defect for the NO_2 group.

Near the pile-up at the center of each transition there was one line for each group of $J\rightarrow J+1$ transitions which was well separated from the rest and was easy to identify as the $J, K=0, k_1=0 (J, \beta=0, I=1)\rightarrow J+1$, $K=0, k_1=0 (J+1, \beta=0, I=1)$ transition. It was found that when a particular value of $A(NO_2)$ was selected, a V_6 could be found such that all of these (0, 0) lines were in agreement with calculations. Thus V_6 was found as a function of $A(NO_2)$. The parameter $A(NO_2)$, neglecting vibration–rotation interaction, is just a function of the O–O distance,

$$A(NO_2)=\tfrac{1}{2}m_O d_{O-O}^2.$$

The relationship between V_6 and d_{O-O} or $A(NO_2)$, is shown in Fig. 1. All subsequent calculations were made consistent with this relationship.

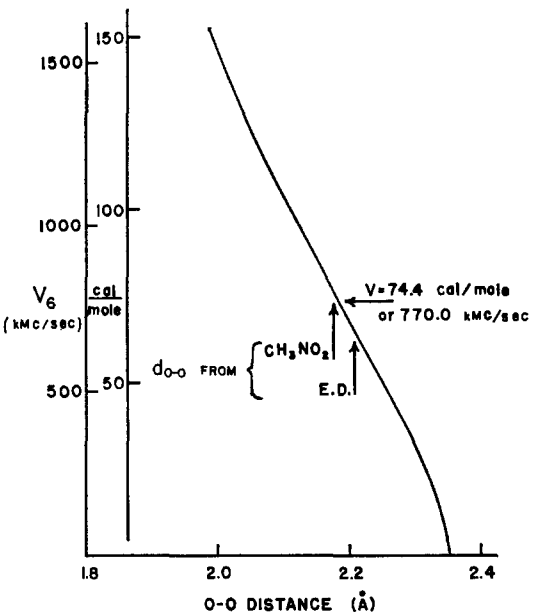

FIG. 1. Relationship between V_6 and O–O distance as determined by requiring agreement with the assigned $J\rightarrow J+1$ (0, 0) lines. The value finally selected is indicated by the arrow labeled 74.4 cal. The value of the O–O distance as determined by electron diffraction by Karle and Karle, Ref. 3, is indicated by the arrow labeled E.D. and the O–O distance found in nitromethane, Ref. 1, is labeled CH_3NO_2.

In the previous work on the spectrum of CH_3NO_2[1] it had been found that most lines were insensitive to the value of the barrier. The four $k_1=\pm 3$, $K=\pm 3$ lines involved pairs of nearly degenerate levels which are connected by large matrix elements proportional to the barrier height. The frequencies of these lines were very sensitive to the value of the barrier and permitted a precise determination of the barrier. Since these lines were so important in CH_3NO_2, a search was made for them. Initially, it was not possible to identify them. The method of determining the remaining variable was thus dependent upon the lines near the center of each $J\rightarrow J+1$ transition, those rather insensitive to the barrier. Calculations were made assuming a barrier height ranging from zero to 100 cal/mole. These indicated that there was no unique value of the barrier which gave an assignment with the agreement which is customary in microwave spectroscopy. After the barrier was determined by the method described in the next section, the $K=\pm 3$, $k_1=\pm 3$ lines were observed. It was found for barriers as high as 70 cm^{-1} that these lines were no longer sensitive to the value of the barrier, but instead, they appeared as partially resolved pairs separated by a distance approximately $B-C$ from the central pile-up. With this knowledge it was then possible to find and identify these lines, but their measurement did not permit a determination of the barrier.

TABLE I. Stark effect of CF_3NO_2.

Transition	M	Calculated Stark coefficient $V=0$	Experimental $\Delta\nu/E^2$[(Mc/sec) cm^2/V^2]	μ debye (Assuming $V=0$)	Calculated Stark coefficient $V=74.4$ cal/mole	μ (debye) (Assuming $V=74.4$ cal/mole)
1→2(0, 0)	0	$-3.099\times10^{-5}\mu^2E^2$	-1.611×10^{-5}	1.432	-3.093×10^{-5}	1.433
	1	2.517	1.410	1.486	2.521	1.485
3→4(0, 0)	0	−0.1880	−0.0987	1.449	−0.1804	1.469
	1	−0.1146	−0.0607	1.445	−0.1080	1.489
	2	0.1060	0.0537	1.414	0.1094	1.392
	3	0.4732	0.2338	1.396	0.4716	1.398
4→5(0, 0)	1	−0.0678	−0.0437	1.594	−0.0808	1.461
	2	−0.0011	−0.0063	4.753	−0.0125	1.409
	3	0.1103	0.0534	1.382	0.1012	1.443
						Av=1.442±0.033

STARK EFFECT AND BARRIER

The assignment of the $K=0$, $k_1=0$ (0, 0) lines was certain, and the Stark coefficients for nine components from three of these lines were measured. Stark coefficients were calculated in the usual manner with the computer. The agreement for most Stark lobes is satisfactory if a zero barrier to internal rotation is assumed. A comparison between the calculated and observed Stark effect is presented in Table I in Columns 3, 4, and 5. The outstanding discrepancy of the $M=2$ component of the 4→5 (0, 0) transition caused us to look more carefully at the dependence of the Stark effect upon a barrier. The observed coefficient for this component is about 10 times as large as that calculated on the basis of a zero potential barrier and the dipole moment as determined from the other transitions. This discrepancy, though apparently large, is magnified by the fact that this coefficient is nearly zero. The Stark[9] effect for any second-order component with quantum number M, can be expressed as $\Delta\nu=(A+BM^2)\mu^2E^2$, where μ is the dipole moment and E the electric field. Values calculated for A and B indicate that $A\cong-4B$ at zero barrier. In calculations with a nonzero barrier, Stark interactions connect two pairs of levels which become nearly degenerate at certain barrier heights. These are the $J=4$, $K=\pm2$, $k=0$ (±2, 0) level with the $J=5$ (0, 0) level, and the $J=3$ (±2, 0) level with the $J=4$ (0, 0) level. These interactions between nearly degenerate levels lead to small variations in the calculated values of A and B. Because of the near cancellation the value of $A+4B$ is very dependent upon the value of the height of the barrier.

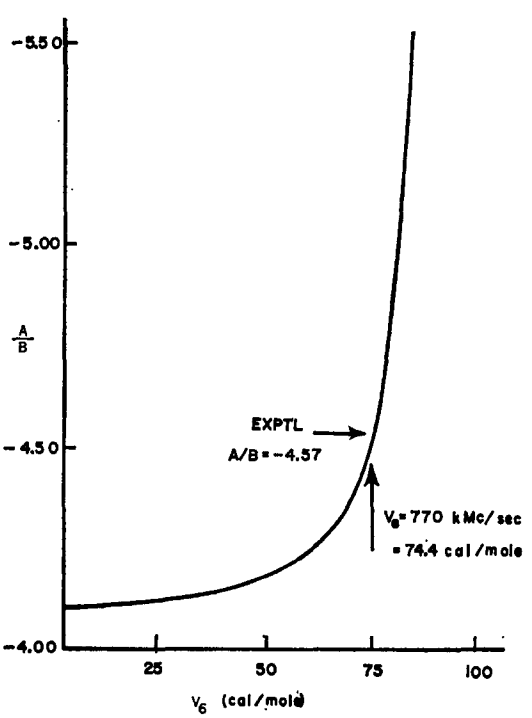

FIG. 2. Ratio of A to B for second-order Stark effect of $J=4(0, 0)\rightarrow J=5(0,0)$ line, $M=2$ component.

The results of A/B calculated for various values of the barrier are plotted in Fig. 2. From the experimental value of A/B of −4.57 the barrier to internal rotation in CF_3NO_2 is found to be 780 kMc/sec or 74.4±5 cal/mole.

For barriers above 80 cal/mole the near degeneracy becomes closer until the Stark effect becomes first order. At still higher barriers the Stark effect again becomes second order, but the value of A/B is less than that for the case of a free rotor and A/B approaches the free rotor value at barrier heights greater than 150 cal/mole.

The barrier obtained by choosing that value which gives the best agreement with experiment is 74.4±5 cal/mole. The calculated Stark effect of this line without a barrier (dotted line) and with a barrier of 74.4 cal/mole (solid line), is compared with the experimental points in Fig. 3. The dipole moment calculated with this value of the barrier is 1.44±0.03 D.

[9] S. Golden and E. B. Wilson, J. Chem. Phys. **16**, 699 (1948).

TABLE II. Calculated vs observed spectrum for CF_3NO_2.

β	$I \rightarrow I'$	Calculated frequency (Mc/sec)	Observed frequency (Mc/sec)
	$J=1 \rightarrow J=2$		
0	1 1	9811.57	9811.6±0.1
1	1 1	9819.90	9820.0±0.2
1	2 2	9849.65	(9851.5 Weak)
2	2 5	9840.62	(Not assigned)[a]
3	1 1	9418.74	9418.8 Broad
	3 3	9419.50	
	2 2	10250.54	10248.24 or
	4 4	10250.42	10250.40
	5 5	9827.45	(Not assigned)
	7 7	9828.77	(Not assigned)
	6 6	9840.40	(Not assigned)
	8 8	9842.58	(Not assigned)
	$J=2 \rightarrow J=3$		
0	1 1	14659.68	14659.83±0.1
	3 3	14844.59	14844.7±0.2
1	1 1	14670.51	14670.6±0.2
	3 2	14783.65	14783.9±0.2
2	1 1	14706.21	14706.1±0.2
	3 3	14807.93	(Not assigned)
	4 4	14724.27	(Not assigned)
	5 5	14775.45	14772.9±0.1
	$J=3 \rightarrow J=4$		
0	1 1	19440.90	19440.85±0.03
	2 2	19642.59	19642.1±0.2
	3 3	19871.13	19871.1±0.1
	10 6	19680.01	19680±0.3
1	1 1	19452.11	19452.3±0.1
	2 2	19761.51	(Not assigned)
	3 3	19733.11	19732±2
	4 4	19729.61	(Not assigned)
	5 5	19640.50	19640.3±0.2
	6 6	19686.14	(Not assigned)
2	1 1	19489.24	19489.1
	3 2	19641.20	(Not assigned)
2	5 3	19894.02	19890±2
	6 4	19592.14	19592±2
	7 5	19727.54	19724±2
	10 6	19688.62	(Not assigned)
3	1 1	19552.47	(Not assigned)
	2 2	19574.49	19578±2
	3 3	18953.01	18950±5
	5 5	18828.05	18825±5
	4 4	20594.57	(Not assigned)
	6 6	24089.60	(Not assigned)
	$J=4 \rightarrow J=5$		
0	1 1	24139.74	24139.64±0.02
	2 2	24510.18	24513±3
	3 3	24956.71	24960±2
	4 5	24661.48	24662±3
	5 5	24662.01	
	6 6		
	6 7		
	7 6	24552.31	(Not assigned)
	7 7		
1	1 1	24148.68	24148.9±2
	2 2	24721.06	(Not assigned)
	3 3	24718.32	24716.5±2
	7 5	24508.70	24503±3
	9 6	24626.38	24622.5±3[b]
2	1 1	24178.29	(Not assigned)
	2 2	24750.05	(Not assigned)
	3 3	24522.30	24525±2
	4 4	24385.86	(Not assigned)
	6 6	24426.21	24423±3
	7 7	24702.03	24696.5±2
	9 9	24550.03	(Not assigned)
	10 10	24628.96	24622.5±3[b]
3	1 1	24199.23	(Not assigned)
	2 2	24272.60	(Not assigned)
	5 3	23868.41	(Not assigned)
	6 4	25821.37	(Not assigned)
	7 5	23524.99	(Not assigned)
	8 6	25601.26	(Not assigned)

[a] "Not assigned" means that no choice could be made among several transitions observed close to the calculated frequency.
[b] This may be $\beta=1$, 9→6 or $\beta=2$, 10→10 line, or both.

Due to the sensitive behavior of the Stark effect as related to the near degeneracy of energy levels, it was important to investigate the validity of two previous assumptions: (1) the fact that the spectrum is insensitive to the value of $A(CF_3)$, and (2) the inertial defect is zero. For a change in the value of $A(CF_3)$ of 4%, the value of A/B changes by slightly less than 1%. An inertial defect was introduced by increasing the value of $A(NO_2)$ by 40 Mc/sec, a value not unreasonable as compared to the value selected for CH_3NO_2. This changed the value of A/B by 0.6%. From these calculations, it is felt that neither assumption places restrictions on the behavior of the Stark effect calculated.

Assuming a value of 74.4 cal/mole for the barrier, the complete spectrum can be calculated and a new comparison made. The calculated vs observed spectrum is presented in Table II for the four lowest J transitions observed. The calculated lines in this table include all of those which are strong enough to be seen and which are far enough from the center pile-ups to be resolved. The agreement is not perfect, though there appears to be good correspondence for some 20 lines. The fact that some lines are not assigned does not

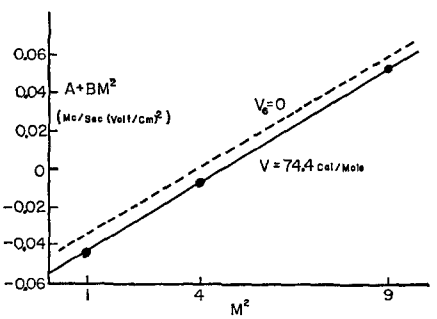

FIG. 3. Stark effect of $J=4(0, 0) \rightarrow J=5(0,)$ line. Dotted line: calculated, assuming $V_6=0$. Solid line: calculated, $V_6=74.4$ cal/mole. The three observed points are plotted assuming a dipole moment of 1.44 D.

TABLE III. Rotational constants and barrier to internal rotation for CF_3NO_2.

$B+C=4917.4\pm0.4$
$B-C=452.8\pm5$
$A(NO_2)=13237\pm150$
$A(CF_3)=5700$ (assumed)
$V_6=780\,000$ Mc/sec$=74.4$ cal/mole

mean an assignment is lacking. In most cases where lines were not assigned, there were lines within 10 Mc/sec, but the identification of them was not definite.

With refined calculations it is found that the center of the pile-up of lines does not fall exactly on a multiple of $B+C$ as would have been expected for the "ideal" case with no centrifugal distortion. The calculated center of the 1→2 transition which gives the best agreement with observed lines is at 9834.8 Mc/sec, while the maximum for the bunching of lines of this transition is experimentally found to be at 9832.0 Mc/sec. This difference can be explained with a centrifugal distortion term.

Several refinements might now be added to our calculations. For example, small correction terms could be added to the Hamiltonian to account for centrifugal distortion, and for a 12-fold barrier. The effect of an inertial defect could be considered by varying the $A(NO_2)$ rotational constant independently of $B-C$. These refinements were made in the cases of nitromethane and methyl boron difluoride and yet small discrepancies remained. For trifluoronitromethane it was felt that these refinements would be of dubious value and the results would not justify the enormous amount of computer time required.

It is also possible to determine the barrier by assuming a value of the O–O distance in the NO_2 group; this determines $A(NO_2)$ and $B-C$. The barrier may then be determined from Fig. 1. Doing this, the barrier is found to be 66 ± 4 cal/mole assuming the O–O distance of 2.21 ± 0.01 Å as determined for trifluoronitromethane by electron diffraction,[3] and 76.6 cal/mole if the value of the O–O distance is taken to be 2.18 A as found in microwave studies on nitromethane.[1] These alternate values are considered to be in good agreement but less reliable than the value of 74.4 ± 5 cal/mole as determined from the Stark effect.

Taking the height of the barrier as being 74.4 cal/mole, $A(NO_2)$ is then found to be 13205 Mc/sec. From this the O–O distance is found to be 2.186 Å (corresponding to an ONO angle of 127° if the NO distance is taken to be 1.22 A).[10]

The moments of inertia I_B and I_C, as determined from the rotational constants B and C, are $I_B=188.20$ and $I_C=226.48$ amu·Å^2. These are not sufficient to determine the structure of trifluoronitromethane. They do, however, permit precise tests of any other structures proposed. As such they are inconsistent with the structure proposed in Ref. 3. Using the C–F distance of 1.325 Å and FCN angle of 109°, as determined from electron diffraction,[3] and the NO distance 1.22 Å and ONO angle of 127° as above, the CN distance may be determined from I_B. This is found to be 1.490 Å, in contrast to the long CN distance of 1.56 Å as proposed in Ref. 3.

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[10] L. E. Sutton, *Tables of Interatomic Distances and Configuration in Molecules and Ions* (The Chemical Society, London, 1958).